

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01D 39/08, 39/16, C08F 2/32	A1	(11) International Publication Number: WO 97/37745 (43) International Publication Date: 16 October 1997 (16.10.97)
(21) International Application Number: PCT/US97/06277 (22) International Filing Date: 4 April 1997 (04.04.97) (30) Priority Data: 60/014,997 8 April 1996 (08.04.96) US (71) Applicant (for all designated States except US): SHELL OIL COMPANY [US/US]; Intellectual Property, 900 Louisiana, P.O. Box 2463, Houston, TX 77252-2463 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): CHANG, Benjamin, Tai, An [US/US]; 14742 Oak Bend Drive, Houston, TX 77079 (US). WONG, Pui, Kwan [US/US]; 6431 Mercer, Houston, TX 77005 (US). MAI, Trong, Van [US/US]; 11658 Evesborough Drive, Houston, TX 77099 (US). (74) Agent: CHRISTENSEN, Del, S.; Shell Oil Company, Intellectual Property, 900 Louisiana, P.O. Box 2463, Houston, TX 77252-2463 (US).		(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: FOAM FILTER MATERIAL AND PROCESS TO PREPARE FOAM FILTER MATERIAL (57) Abstract A method is provided to prepare a filter material, the method comprising the steps of: providing a porous substrate; preparing a high internal phase emulsion wherein the external phase of the emulsion comprises polymerizable monomers, and the internal phase is a non-polymerizable phase; impregnating the high internal phase emulsion into the substrate felt; and polymerizing the polymerizable monomers. A layer of cured foam as is thereby formed on the substrate and within pore volumes of the substrate. The cured foam can have a high porosity, small pore size, and low density, resulting in a filter material having a high efficiency in removal of particles, at a lower pressure drop than alternative high efficiency filter materials.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

DESCRIPTIONFOAM FILTER MATERIAL AND PROCESS TO PREPARE
FOAM FILTER MATERIALTechnical Field

5 This invention relates to a foam impregnated
filter material and a process to prepare such a material.

Background Art

10 Polyester felts, usually melt blown, are known to
be useful filter materials for applications such as bag
filters. These materials are relatively inexpensive, but
have relatively large pore sizes because of the diameter
polyester threads necessary to result in a sufficiently
strong filter material. U.S. Pat. No. 5,205,938 suggests
a polyester filter material that is improved by providing
a graded pore size. But the porosity of the resultant
15 material can not be as low as what is desired because a high
density of fibers is needed to provide sufficiently small
volumes between fibers. Very small diameter fibers could
theoretically be used to achieve a small pore size with
similar densities, but such small fibers are exceedingly
20 difficult to produce and handle. This density, or porosity,
results in a greater pressure drop that is desirable.

U.S. Pat. No. 5,318,831 suggests that a small pore
size can be achieved by laminating a needle layer to a
nonwoven fabric sheet. The needle layer is made of ultra
25 fine fibers. Significant strength is imparted by the
nonwoven fabric sheet. A small pore size is still achieved
in a felt type of material because of the ultra fine fibers,
but the filter material has a greater than desirable
density.

30 Another commercially available filter material
consists of a membrane of polytetrafluoroethylene resin
laminated to the surface of a felt substrate. This type of
membrane can have very small pore openings. The resin
membrane is stretched to form small voids within the
35 membrane. The voids can be very small, but the void volume
of the membrane is not large, and a significant pressure

drop is incurred by a stream passing through the membrane. Further, this type of filter material is relatively expensive, and the resin membrane is prone to breakage.

It would be desirable to provide a filter material wherein a high porosity can be achieved along with a small pore size in a filter layer, thereby minimizing pressure drop through the filter material.

Polymeric open cell foams are used in air and water filters in applications such as air filters for lawn mowers and aircraft. Some of these filters, for example, BRACKET® aircraft air filters, include a plurality of layers of decreasing pore size foam. These filters trap particles within the volume of the foam, and therefore it is difficult to remove the particles from the filter. These filters are not strong enough to be used as filter material in, for example, bag house filters.

Low density foams are porous crosslinked polymer blocks. Such low density porous polymer blocks can be prepared by polymerizing a specific type of water-in-oil emulsion known as high internal phase emulsion having relatively small amounts of a continuous oil phase, the oil phase containing polymerizable monomers, and relatively greater amounts of an internal water phase.

Such low density foams are prepared by a process disclosed in U.S. Pat. No. 4,522,953 by polymerizing and crosslinking monomers in the continuous oil phase of a high internal phase water-in-oil emulsion with a polymerization initiator such as potassium persulfate. Generally, these high internal phase water-in-oil emulsions contain at least 90 weight percent of a water phase as the internal phase. The high ratio water-in-oil emulsions are formed by combining the oil phase with water under moderate shear. In order to obtain this high internal phase water-in-oil emulsion, a surfactant is used to stabilize the emulsion. It is also advantageous to incorporate an electrolyte into the aqueous phase. The amount and type of electrolyte, along with the amount and type of surfactant, effects the

pore size, and hydrophobic/hydrophilic character of the cured foam.

Composite foams are disclosed in U.S. Pat. No. 5,037,859. These foams are prepared by first preparing a rigid foam, the rigid foam being a rigid open cell foam, such as a polystyrene foam. The first rigid foam has a relatively large pore size. A second emulsion is then forced into the first rigid foam to form a smaller pore diameter foam within the polystyrene. The resultant composite foams have greater strengths and densities than foams produced from only the second emulsion. The resultant composite foams also retain the better wicking properties of the first foam, but the resultant composite foam is stiff, inflexible, and brittle. It is therefore not an acceptable material for uses such as bag house filters.

It is therefore an object, in one aspect of the present invention, to provide a method to prepare filter materials using a flexible substrate, and a foam cured from high internal phase emulsions impregnated in the felt and/or as a layer along with the substrate. In another aspect, it is an object to provide a filter material having a flexible substrate impregnated with a foam material, the foam material having a mean average pore size in the range of about one to about 100 microns. In another aspect of the present invention, it is an object to provide a filter material by the method of the present invention. In another aspect of the present invention it is an object to provide such a filter material having, in the portion of the material that is foam, an average pore diameter in the range of about one to about 100 micron and a density of less than about 0.2 gm/cc.

Description of the Invention

According to the invention, a filter material is prepared by a method, the method comprising the steps of:

- providing a flexible porous substrate material;
- preparing a high internal phase emulsion wherein the external phase of the emulsion comprises polymerizable

hydrocarbon monomers, and the internal phase is an aqueous phase;

impregnating the high internal phase emulsion into the substrate material; and

5 polymerizing the polymerizable hydrocarbon monomers.

The foam material within the felt substrate can be prepared with mean pore sizes of between about one and about one hundred microns, and with densities of the foam phase of less than about 0.2 gm/cc. These materials, because of
10 a very high porosity and a small pore size of the foam portion of the filter materials, impart minimal pressure drops to streams passing through the filter. These filter materials are also prepared from inexpensive materials.

Detailed Description of the Preferred Embodiments

15 Substrates of the present invention may be woven or non-woven materials, including knitted and needle-punched felts. Non-woven materials are preferred because of their generally lower costs and higher porosities. The substrate materials may be made of either organic or inorganic fibers,
20 or combinations thereof.

A substrate for the filter material of the present invention may be one of many available felts of natural or synthetic fibers. Polyester felt is commonly used, and is acceptable in the practice of the present invention. Such
25 a felt substrate is of a relatively open structure, and serves to provide strength to the final filter material.

The substrate of the present invention initially has a porosity, and a volume average pore size greater than that desired of the final filter material. The polymerized
30 foam material of the present invention fills some of the pore volumes with interconnected pores of a smaller size, but a relatively consistent and predictable size that is considerably smaller than the pore size that can be achieved in a woven or nonwoven fabric.

35 The polymeric foam is provided in the substrate, or as a layer on the substrate, by forming an emulsion of an external phase containing polymerizable monomers and a

surfactant, and an internal phase. With careful selection of surfactants, acceptable emulsions of polymerizable hydrocarbons and an aqueous phase can contain aqueous phase to hydrocarbon ratios of 30 to 60, resulting in a very open-celled and light final foam composition.

The emulsion can be applied to the substrate as a film, and can be impregnated into the substrate by, for example, pressing the emulsion into the substrate with rollers or by pressing the substrate and emulsion between plates. When the emulsion is cured as a layer on the substrate, pressing a portion of the emulsion into the substrate helps provide good adhesion between the substrate and the cured foam layer.

It is important that the surfaces of the cured foams remain as open celled foams. It has been found that a non-porous "skin" will form at the surface of the foam if the emulsion is cured exposed to non-polar materials. It is therefore important that the emulsion be cured with the emulsion surfaces contacting a polar surface (such as MYLAR® film or glass) or water.

The emulsion preferably forms as a layer of about four to about eight mils in thickness over the substrate, with the foam penetrating at least partially into the substrate to ensure good adhesion thereto.

Although the present invention is described in greater detail as utilizing an emulsion comprising an aqueous phase of water and a salt, and a hydrocarbon phase comprising polymerizable hydrocarbon monomers and a surfactant, the emulsion could be formed with different combinations of immiscible phases, so long as the external phase contains polymerizable monomers. For example, inorganic soluble salts that precipitate to form an inorganic oxide matrix could be in an aqueous phase with an internal inert hydrocarbon phase. Alternatively, water soluble polymerizable monomers could be provided in an external aqueous phase, such as phenol-formaldehyde or resorcinol-formaldehyde. The two phases could be immiscible

organic phases, with polymerizable monomers in one phase. For example, phenolic foams could be formed by a two phase mixture of hexane in aqueous phenol-formaldehyde resin.

5 An emulsion according to the present invention can be produced by forming a curable water-in-oil high internal phase emulsion by gradually adding and mixing an aqueous solution optionally containing an electrolyte into a monomer solution (oil phase) containing a mixture of polymerizable monomers and a surfactant. A polymerization initiator is
10 added either in the monomer solution or the aqueous solution before mixing or after formation of the emulsion depending on the desired process conditions. The curable water-in-oil high internal phase emulsion is then cured (polymerized and crosslinked) by heating the emulsion to a temperature
15 effective to crosslink and polymerize the monomers and for a time effective to cure the monomers.

The mixture of polymerizable monomers generally contains one or more vinyl monomers and one or more crosslinking agents. Various monomers may be used in the
20 preparation of the foams, provided the monomers can be dispersed in or form an oil phase of a water-in-oil high internal phase emulsion (oil-soluble) and have a polymerizable vinyl group. Suitable vinyl monomers include, for example, monoalkenyl arene monomers such as styrene, α -methylstyrene, chloromethylstyrene, vinyl ethylbenzene and vinyl toluene; acrylate or methacrylate esters such as 2-ethylhexyl acrylate, n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, hexyl acrylate, n-butyl methacrylate, lauryl methacrylate, and isodecyl methacrylate; conjugated
25 diolefins such as butadiene, isoprene, and piperylene; allenes such as allene, methyl allene and chloroallene; olefin halides such as vinyl chloride, vinyl fluoride and polyfluoro-olefins; and mixtures thereof.

Suitable crosslinking agents can be any
35 multifunctional unsaturated monomers capable of reacting with the vinyl monomers. The crosslinking agents contain at least two functional groups. The functionality can be,

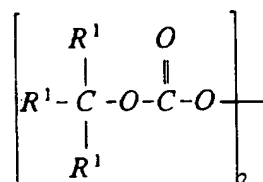
for example, vinyl groups, acrylate groups and methacrylate groups. Multifunctional unsaturated crosslinking monomers include, for example, difunctional unsaturated crosslinking monomers such as divinylbenzene, diethylene glycol dimethacrylate, 1,3-butanediol dimethacrylate, and allyl methacrylate and tri-, tetra- and penta-functional unsaturated crosslinking monomers such as trimethylolpropane trimethacrylate, pentaerythritol tetramethacrylate, trimethylolpropane triacrylate, and pentaerythritol tetraacrylate, glucose pentaacrylate, glucose diethylmercaptal pentaacrylate, and sorbitan triacrylate; and poly-functional unsaturated crosslinking monomers such as polyacrylates (e.g. sucrose per(meth)acrylate and cellulose (meth)acrylate). Crosslinking monomers are typically present in each emulsion in an amount of from about 2 weight percent to about 70 weight percent, preferably from about 5 weight percent to about 40 weight percent based on the total monomer mixture. Some of these crosslinking monomers can be incorporated as a non-crosslinked monomer as long as at least about 2 weight percent of the crosslinking monomers are crosslinked.

Divinylbenzene is a preferred crosslinking monomer, and is typically available as a mixture with ethyl styrene in proportions of about 55:45 by weight. These proportions can be modified so as to enrich the oil phase with one or the other component. Generally, it is advantageous to enrich the mixture with ethyl styrene which simultaneously reducing the amount of styrene in the monomer blend. The preferred ratio of divinylbenzene to ethyl styrene is from about 30:70 to 55:45, most preferably from about 35:65 to about 45:55, by weight. The inclusion of higher levels of ethylstyrene imparts greater toughness without increasing the T_g of the resulting copolymer to the degree that styrene does.

Suitable polymerization initiators can be water-soluble or oil-soluble. Water-soluble initiators include, for example, persulfates such as potassium or sodium

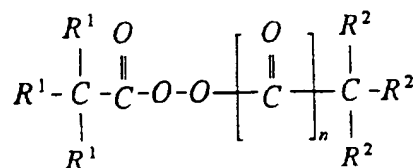
persulfate and various redox systems such as ammonium persulfate together with sodium metabisulfite. Oil soluble (monomer soluble) initiators include, for example, azo compounds such as azobisisobutyro-nitrile; and peroxides
 5 such as benzoyl peroxide, methyl ethyl ketone peroxide, alkylperoxycarbonates such as di-2-ethylhexyl peroxydicarbonate and di(sec-butyl)peroxydicarbonate and alkylperoxycarboxylates such as t-butyl peroxyisobutyrate, 2,5-dimethyl-2,5-bis(2,3-ethylhexanoylperoxy)hexane, and t-butyl
 10 peroctoate. The preferred water-soluble polymerization initiator is potassium persulfate and the preferred oil-soluble polymerization initiators are alkylperoxycarbonates and alkyl-peroxycarboxylates for fast curing time.

Most preferable alkylperoxycarbonates are branched
 15 at the 1-carbon position and most preferable alkylperoxycarboxylates are branched at the α -carbon position and/or 1-carbon position. These branched alkylperoxycarbonate peroxide can be represented by the formula:



where R^1 is independently C_1 to C_{16} hydrocarbons or hydrogen
 20 in which at least two of the R^1 are hydrocarbon groups.

The preferred branched alkyl carboxylate peroxide can be represented by the formula:



$$n=0,1$$

where R^1 and R^2 are independently C_1 to C_{16} hydrocarbon groups or hydrogen in which at least two of the R^1 or R^2 are hydrocarbon groups. Preferably at least two of both R^1 and R^2 are hydrocarbon groups. Hydrocarbon groups can be alkyl, alkenyl or aryl groups.

The water-soluble initiators and/or oil-soluble initiators should be present in an effective amount to cure (polymerize and crosslink) the monomers. Typically the initiator can be present from about 0.005 to about 15 weight percent based on the monomers. The initiators can be introduced with the oil phase or the aqueous phase before or after formation of the high internal phase emulsion.

A water-soluble initiator such as potassium persulfate can be added to the aqueous solution before forming the emulsions or to the emulsions. An oil-soluble initiator can be added to the monomer solution or an advanced monomer solution or to the emulsion. Addition of a polymerization initiator to a high internal phase water-in-oil emulsion is described in U.S. Pat. No. 5,210,104, the disclosure of which is herein incorporated by reference. The initiator added to the emulsion can optionally be blended into the emulsion by any blending technique such as, for example, static mixer or a pin mixer at a low shear rate, to form a curable water-in-oil high internal phase emulsion. The rate of shear must be high enough to blend the initiator but low enough not to allow the emulsion to coalesce or liquify.

Conveniently, the initiators can be added to the oil phase (monomer phase) or aqueous phase prior to formation of the emulsion. Alternatively, at least a portion of the monomer solution can be advanced (partially polymerized) in the presence of an effective amount of an advancement initiator or by a free-radical-producing radiation source to produce an advanced monomer component prior to formation of the emulsion to reduce curing time.

To form a stable high internal phase emulsion requires that a surfactant be included in the emulsion.

Such surfactant must be soluble in the oil phase used to form the emulsion with the internal phase being aqueous. The surfactant may be nonionic, cationic, anionic or amphoteric provided the surfactant or combination of surfactants are effective to form a stable high internal phase emulsion. Preferred types of surfactants that can be used include sorbitan fatty acid esters, polyglycerol fatty acid esters, polyglycerol fatty acid esters, polyoxyethylene fatty acids and esters. In particular, sorbitan fatty acid esters such as sorbitan monolaurate ("SPAN® 20"), sorbitan monooleate ("SPAN® 80"), and combinations of sorbitan trioleate ("SPAN® 85"), and sorbitan monooleate. One such surfactant combination is the combination of sorbitan monooleate and sorbitan trioleate in a weight ration greater than or equal to about 3:1, more preferably about 4:1. Another acceptable surfactant is "TRIODAN® 20" which is a polyglycerol ester available from Grindsted and "EMSORB 252" which is a sorbitan sesquioleate available from Henkel.

Between about one and about thirty percent by weight of surfactant, based on the monomers in the oil phase, is generally sufficient, with higher water to oil ratios and higher mixing and curing temperatures generally requiring more surfactant than lower water to oil ratios and temperatures.

The type of surfactant used in making the high internal phase emulsions that are to be polymerized is important in forming water-in-oil high internal phase emulsion and effects the final properties of the polymerized foams obtained. The surfactants are typically added to the monomer phase (oil phase).

The amount of surfactant system must be such that a water-in-oil high internal phase emulsion will form, and does not break prior to curing being essentially complete. Generally, the surfactant system is present in an amount effective to form a water-in-oil high internal phase emulsion. Preferably, the surfactant system can be present in concentrations of from about 0.1 to about 40 weight

percent, more preferably about one to about thirty weight percent based on the monomers of the particular emulsion. When saccharide fatty acid esters are used as a component of the surfactant the saccharide fatty acid surfactants are preferably present in an amount between about 0.1 weight percent and about 36 weight percent, more preferably from about 0.1 to about 25 weight percent based on the monomers. When sorbitan fatty acid esters are used as a component of the surfactant the sorbitan fatty acid ester surfactants are preferably present from about 2 weight percent to about 36 weight percent, more preferably from about 5 weight percent to about 25 weight percent based on the monomers.

The relative amounts of the aqueous phase containing water and an electrolyte and monomer phase containing monomers and surfactants used to form the high internal phase emulsions are a factor in determining the structural, mechanical and performance properties of the resulting polymeric foam phases. The ratio of water to oil in the emulsions can influence the density, cell size, and specific surface area of the foam phase. To form a polymeric foam phase with suitable density and high porosity, the water-in-oil high internal phase emulsions typically contain as the internal phase, at least about 70 weight percent of water, based on the emulsion, corresponding to a water to oil weight ratio of at least about 7:3, more preferably at least about 90 weight percent of water, most preferably at least about 95 weight percent of water, corresponding to a water to oil weight ratio of at least about 20:1.

The internal aqueous phase preferably contains a water-soluble electrolyte. This water-soluble electrolyte stabilizes the emulsion. Suitable electrolytes include inorganic salts (monovalent, divalent, trivalent or mixtures thereof), for example, alkali metal salts, alkaline earth metal salts and heavy metal salts such as halides, sulfates, carbonates, phosphates and mixtures thereof. Such electrolyte includes, for example, sodium chloride, sodium

sulfate, potassium chloride, potassium sulfate, lithium chloride, magnesium chloride, calcium chloride, magnesium sulfate, aluminum chloride and mixtures thereof. Mono- or di-valent salts with monovalent anions such as halides are preferred.

The formation of a water-in-oil emulsion is described in U.S. Pat. No. 4,522,953, and U.S. Pat. No. 5,149,720, the disclosures of which are incorporated herein by reference. In general, to form the water-in-oil emulsion, the water can be mixed in any way up to a water to oil ratio of about 4:1. An oil-in-water emulsion becomes preferred if the water was added all at once beyond a water to oil ratio of about 4:1. Typically, the water must be added gradually with a moderate rate of shear. A small capacity mixer such as a paint mixer with a shear rate of at least about 5 s^{-1} , preferably at least about 10 s^{-1} can be used to mix the water-in-oil emulsion. A larger mixer equipped with an impeller with a shear rate of at least about 10 s^{-1} or a pin gap mixer with a shear rate of at least about 50 s^{-1} , preferably at least about 100 s^{-1} can also be used. If the shear rate is too low, the water-in-oil emulsion may revert to a oil-in-water emulsion.

A high internal phase emulsion can be prepared in batches or continuously. To form the high internal phase emulsion in batches, the emulsion is formed in a vessel or a container by gradually adding an aqueous phase to a monomer mixture and/or advanced monomer mixture under a moderate rate of shear until the desired water to oil ratio is reached.

A high internal phase emulsion can be prepared continuously by initially preparing a preformed emulsion of approximately the same character as the desired emulsion by the method described above, then introducing into the preformed emulsion, both the aqueous phase and/or the oil phase in such proportions so as to produce the desired emulsion. The emulsified mass is maintained in a state of continuous shear. The shear is sufficient to reduce the

effective viscosity of the mass to about the effective viscosity of the introduced phase but not above the inherent shear stability point of the desired emulsion. The prepared emulsion is then withdrawn at the desired rate.

5 The aqueous phase and the monomer phase for the batch process and the continuous process can be introduced in a mixing vessel by an aqueous stream or a monomer stream, respectively, through one or more inlets. The streams can be combined prior to or after entering the mixing vessel.
10 then mixed in such a way to produce the desired emulsion. The mixing vessel is any container in which the high internal phase emulsion is made regardless of the type of mixer or mixer head used.

15 The curable water-in-oil high internal phase emulsions can be cured in a batch process or in a continuous process. The emulsion or aqueous stream or monomer stream can be heated prior to or after the addition of the initiator.

20 The emulsion is preferably polymerized and cured at a temperature within the range of about 25°C to about 90°C, as long as the emulsion is stable at the curing temperature. Alternatively, a multiple-step process can be used. Such a multiple-step process is described in U.S. Pat. No. 5,189,070 issued February 23, 1993, the disclosure
25 of which is herein incorporated by reference. In the multi-step process the emulsion is pre-cured at a temperature of less than about 65°C until the emulsion has a Rheometrics dynamic shear modulus of greater than about 500 pascal, (lightly gelled, having a consistency like a jelly or a
30 gelatin referred to as "gel"), then cured at a temperature of above about 70°C for a time effective to cure the gel. The cure can be as high as about 175°C under a pressure sufficient to prevent the aqueous phase from boiling.

35 The emulsions can be heated, for example, by hot water, hot air, steam, ERR, RF, microwave or ohmic heating. The emulsions should be cured until the desired properties are obtained. Typically, to obtain a cured foam, the

emulsions should be cured for at least about 8 hours, at 60°C or at least about 1 hour at 60°C then 3 hours at a temperature of above about 70°C. Generally, the extent of reaction after curing is at least about 85% of the monomers, preferably at least about 90%, more preferably at least about 95% (i.e., less than about 5% free monomers remaining), most preferably at least about 99% (i.e., less than about 1% free monomers remaining) in order to obtain good properties.

These foams can be optionally post-cured to improve the foam properties. Post-curing of the foam can be carried out by heating the foams at a temperature of above about 75°C, preferably greater than 90°C by steam, hot air, or other heating source. Such heating may be performed initially in a heat exchanger, oven, over heated rollers or by other means.

When the temperature is near or above the boiling point of water, pressure is preferably applied to keep the water in the liquid phase. Pressure can be applied to the emulsion, if desired, at a pressure generally from above atmospheric pressure, typically within the range of about atmospheric pressure to about 1.03 MPa (150 psig). When the temperature is about 100°C, a pressure from about 7 to 70 kPa gauge (about 1 to 10 psig) is sufficient; when the temperature is about 130°C, a pressure from about 210 to 480 kPa gauge (about 30 psig to 70 psig) is preferred. The preferred pressures will be from just above the autogenous steam pressure of the solution to about twice that absolute pressure.

For example, the emulsion can be cured under pressure by using an autoclave operating under autogenous pressure of steam generated from pure water at a given temperature, by applying nitrogen or air pressure to prevent boiling of the emulsion or by mechanical means, such as rollers, pistons, molds, or the like.

Once the curing and/or post-curing process is completed, the water incorporated in the foam may be removed

or squeezed out, dried by heat or flashed by lowering the pressure to a suitable level to evaporate the remaining liquid to give the desired degree of dryness in the product foam. These drying techniques will preferably be used after
5 the desired state of cure is developed in the foam material.

The foam containing filter material of the present invention may be washed prior to, after or between drying stages (removing at least a portion of the water). Typically, these foams are washed to reduce the electrolyte
10 content of the foam with a solvent such as, for example, an alcohol, a low concentration electrolyte solution (lower concentration than the water phase) such as 1% calcium chloride solution or deionized water. The washed foams can be conveniently dried by squeezing the water and/or solvent
15 out of the foams and air or heat drying.

The foams produced by the inventive process possess high porosities, low densities, small pore size, and uniform properties especially suitable for use as a filter material for, for example, bag house filters.

20 Illustrative Embodiment

The following illustrative embodiments describe the process of the invention and are provided for illustrative purposes and do not limit the present invention.

25 All reagents and solvents used in the following examples were technical or reagent grade and were used without further purification unless otherwise noted. Divinylbenzene was 55% pure and contained a mixture of isomers. The inhibitor, t-butyl catechol, in both styrene
30 and divinylbenzene remained present for the reaction.

TESTING METHODS

AIR PERMEABILITY TEST was performed by Grubb Filtration Testing Services of Delran, New Jersey. ASTM D737 was the test procedure. In this test, the flow rate
35 of air passing through the filter is measured at a differential pressure of one half inch of water.

AIR FILTRATION EFFICIENCY TEST was performed by the University of Tennessee at Knoxville, Tennessee. ASTM F1215 was the test procedure. An average dust particle size of one tenths of a micron was used.

5 EXAMPLE 1

 A substrate of Lantor 16 oz/yd² #1625 polyester felt, 0.0625 inches thick was used. An emulsion was prepared having a water to hydrocarbon weight ratio of 50. The hydrocarbon phase of the emulsion was 20 parts by weight
10 styrene, 20 parts by weight divinylbenzene, 60 parts by weight ethylhexylacrylate, and 12 parts by weight SPAN® 20. The water contained ten percent by weight, based on the water phase, of calcium chloride and two tenths of a percent by weight potassium persulfate as an initiator for the
15 polymerization. The water phase was slowly added to the oil phase as the mixture was stirred with a paint stirrer. An emulsion formed. The emulsion was then spread over a mylar sheet, and a felt placed over the emulsion. The weight ratio of emulsion to felt was about 1.5. A glass plate was
20 then pressed onto the top of the felt to press a portion of the emulsion into the felt. The glass was then removed and the top of the felt wetted with water. The glass plate was then replaced with the space outside of the felt sealed with a rubber rope. The emulsion was then cured at about 60°C
25 for fifteen hours. A foam of a thickness of about one hundred to two hundred microns in thickness was formed at the surface of the felt, and was firmly attached to the felt.

 Porosity of the foam phase, based on the weight
30 ratio of water to oil, was about 98%. Average pore size of the foam phases would be expected to be about 40 microns.

 Filtration efficiency for the resultant product was 69% for an average dust particle size of 0.1 micron, and flow through the filter was 18.4 ft³/min per ft² under a
35 differential pressure of 0.5 inch water.

For comparison, filtration efficiency and flow rate tests were performed on commercially available filter materials and the results are listed below in the TABLE.

TABLE

5	COATING MATERIAL	FILTER MATERIAL	POROSITY	FLOW RATE CFM	EFFICIENCY
	NONE	LANTOR 16 oz	78%	29.8	28
	ACRYLIC FOAM	LANTOR PE-1000		26.5	29
10	ACRYLIC FOAM	LANTOR PE-1001		38.5	30
	PTFE	GORETEX 16 oz	82%	9.88	99
	PTFE	TETRATEX 6202		7.45	99
	PTFE	TETRATEX 6212		8.65	97
15	PTFE	TETRATEX 6214		13.4	92

As can be seen from the TABLE, compared to the results of the example, greater efficiency can be achieved with polyterafloroethylene filter materials, but only with a significant increase in pressure drop (or increase in surface area of the filter), and the cost of providing the PTFE is considerably greater than the filter material of the present invention. Other filters materials have considerably larger pore sizes, and as a result, are of significantly lower filtration efficiency. The present invention results in a filter medium of high efficiency, and considerably higher efficiency than other materials of similar cost.

CLAIMS

1. A method to prepare a filter material, the method comprising the steps of:

providing a porous substrate;

5 preparing a high internal phase emulsion wherein the external phase of the emulsion comprises polymerizable monomers, and the internal phase is an immiscible non-polymerizable phase;

10 impregnating at least a portion of the high internal phase emulsion into the substrate; and
polymerizing the polymerizable monomers.

2. The method of claim 1 wherein the immiscible non-polymerizable phase is an aqueous phase.

15 3. The method of claim 2 wherein the polymerizable monomers comprise one or more vinyl monomer and one or more crosslinking agent.

4. The method of claim 3 wherein the vinyl monomer is selected from the group consisting of styrene, α -methylstyrene, chloromethylstyrene, vinyl ethylbenzene, vinyl toluene, 2-ethylhexyl acrylate, n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, hexyl acrylate, n-butyl methacrylate, lauryl methacrylate, isodecyl methacrylate, butadiene, isoprene, piperylene, allene, methyl allene, chloroallene, vinyl chloride, vinyl fluoride, polyfluoro-
25 olefins, and combinations thereof.

5. The method of claim 3 wherein the crosslinking agent contains at least two functional groups, the functional groups selected from the group consisting of vinyl groups, acrylate groups and methacrylate groups.

30 6. The method of claim 5 wherein the crosslinking agent is a multifunctional unsaturated monomers capable of reacting with the monomers, the crosslinking agents are selected from the group consisting of divinylbenzene, diethylene glycol dimethacrylate, 1,3-butanediol dimethacrylate, trimethylolpropane trimethacrylate, pentaerythritol tetramethacrylate, trimethylolpropane triacrylate, pentaerythritol tetraacrylate, glucose
35

pentaacrylate, glucose diethylmercaptal pentaacrylate, sorbitan triacrylate, sucrose per(meth)acrylate and cellulose (meth)acrylate.

5 7. The method of claim 3 wherein the substrate is a polyester felt.

8. The method of claim 3 wherein the phase containing the polymerizable monomers further comprises a surfactant selected from the group consisting of sorbitan fatty acid esters, polyglycerol fatty acid esters,
10 polyglycerol fatty acid esters, polyoxyethylene fatty acids and esters and combinations thereof.

9. The method of claim 8 wherein the aqueous phase further comprises a free-radical initiator effective to initiate polymerization of the polymerizable monomers.

15 10. A filter material prepared by a method, the method comprising the steps of:

providing a felt substrate material;

preparing a high internal phase emulsion wherein the external phase of the emulsion comprises polymerizable
20 monomers, and the internal phase is an immiscible non-polymerizable phase;

impregnating the high internal phase emulsion into the felt; and

polymerizing the polymerizable monomers.

25 11. The filter material of claim 10 wherein the immiscible non-polymerizable phase is an aqueous phase.

12. The filter material of claim 11 wherein the polymerizable monomers comprise one or more vinyl monomer and one or more crosslinking agent.

30 13. The filter material of claim 12 wherein the vinyl monomer is selected from the group consisting of styrene, α -methylstyrene, chloromethylstyrene, vinyl ethylbenzene, vinyl toluene, 2-ethylhexyl acrylate, n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, hexyl acrylate, n-butyl
35 methacrylate, lauryl methacrylate, isodecyl methacrylate, butadiene, isoprene, piperylene, allene, methyl allene,

chloroallene, vinyl chloride, vinyl fluoride, polyfluoro-olefins, and combinations thereof.

14. The filter material of claim 12 wherein the crosslinking agent contains at least two functional groups, the functional groups selected from the group consisting of vinyl groups, acrylate groups and methacrylate groups.

15. The filter material of claim 14 wherein the crosslinking agent is a multifunctional unsaturated monomers capable of reacting with the monomers, the crosslinking agents are selected from the group consisting of divinylbenzene, diethylene glycol dimethacrylate, 1,3-butanediol dimethacrylate, trimethylolpropane trimethacrylate, pentaerythritol tetramethacrylate, trimethylolpropane triacrylate, pentaerythritol tetraacrylate, glucose pentaacrylate, glucose diethylmercaptal pentaacrylate, sorbitan triacrylate, sucrose per(meth)acrylate and cellulose (meth)acrylate.

16. The filter material of claim 12 wherein the phase containing the polymerizable monomers further comprises a surfactant selected from the group consisting of sorbitan fatty acid esters, polyglycerol fatty acid esters, polyglycerol fatty acid esters, polyoxyethylene fatty acids and esters and combinations thereof.

17. The filter material of claim 16 wherein the aqueous phase further comprises a free-radical initiator effective to initiate polymerization of the polymerizable monomers.

18. A foam impregnated material comprising:

a) a flexible substrate material having a plurality of connected void volumes within the material;

b) a polymerized foam material within the void volumes of the substrate, the polymerized material having mean average pore sizes of between about one micron and about one hundred microns.

19. The foam impregnated material of claim 18 wherein the polymerized material comprises polymerized

monomer units of one or more type of vinyl monomer and one or more type of crosslinking agents.

20. The foam impregnated material of claim 19 wherein the polymerizable monomers units selected from the group consisting of styrene, α -methylstyrene, chloromethylstyrene, vinyl ethylbenzene, vinyl toluene, 2-ethylhexyl acrylate, n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, hexyl acrylate, n-butyl methacrylate, lauryl methacrylate, isodecyl methacrylate, butadiene, isoprene, piperylene, allene, methyl allene, chloroallene, vinyl chloride, vinyl fluoride, polyfluoro-olefins.

21. The foam impregnated material of claim 20 wherein the crosslinking agents contain at least two functional groups, the functional groups selected from the group comprising vinyl groups, acrylate groups and methacrylate groups.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/06277

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D39/08 B01D39/16 C08F2/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D C08F C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 137 633 A (WANG DAVID) 11 August 1992 see column 2, line 37 - column 6, line 9; claims 1-16 ---	1,3-7,9, 10, 12-15, 18-21
A	EP 0 299 762 A (UNILEVER PLC ;UNILEVER NV (NL)) 18 January 1989 see the whole document ---	1-6, 9-15, 17-21
A	US 5 334 621 A (BESHOURI SHARON M) 2 August 1994 see claims 1-15 ---	2-6,8,9, 11-17
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

29 July 1997

Date of mailing of the international search report

11. 08. 97

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Cubas Alcaraz, J

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/06277

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 908 236 A (PITT ALDO M ET AL) 13 March 1990 see the whole document ---	1,3-7,9, 10, 12-15, 18-21
A	US 4 855 163 A (JOFFEE IRVING B ET AL) 8 August 1989 see the whole document ---	1-21
A	US 5 037 859 A (WILLIAMS JR JOEL M ET AL) 6 August 1991 cited in the application see the whole document -----	1-21

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/06277

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5137633 A	11-08-92	NONE	
EP 0299762 A	18-01-89	AU 1896588 A JP 2041336 A	19-01-89 09-02-90
US 5334621 A	02-08-94	US 5362762 A	08-11-94
US 4908236 A	13-03-90	US 4917793 A US 5037656 A	17-04-90 06-08-91
US 4855163 A	08-08-89	US 4774132 A AU 596840 B AU 7188087 A BR 8702172 A CA 1302177 A DE 3774323 A EP 0245000 A GB 2190039 A,B JP 2502309 B JP 62267340 A	27-09-88 17-05-90 05-11-87 17-02-88 02-06-92 12-12-91 11-11-87 11-11-87 29-05-96 20-11-87
US 5037859 A	06-08-91	US 4966919 A	30-10-90